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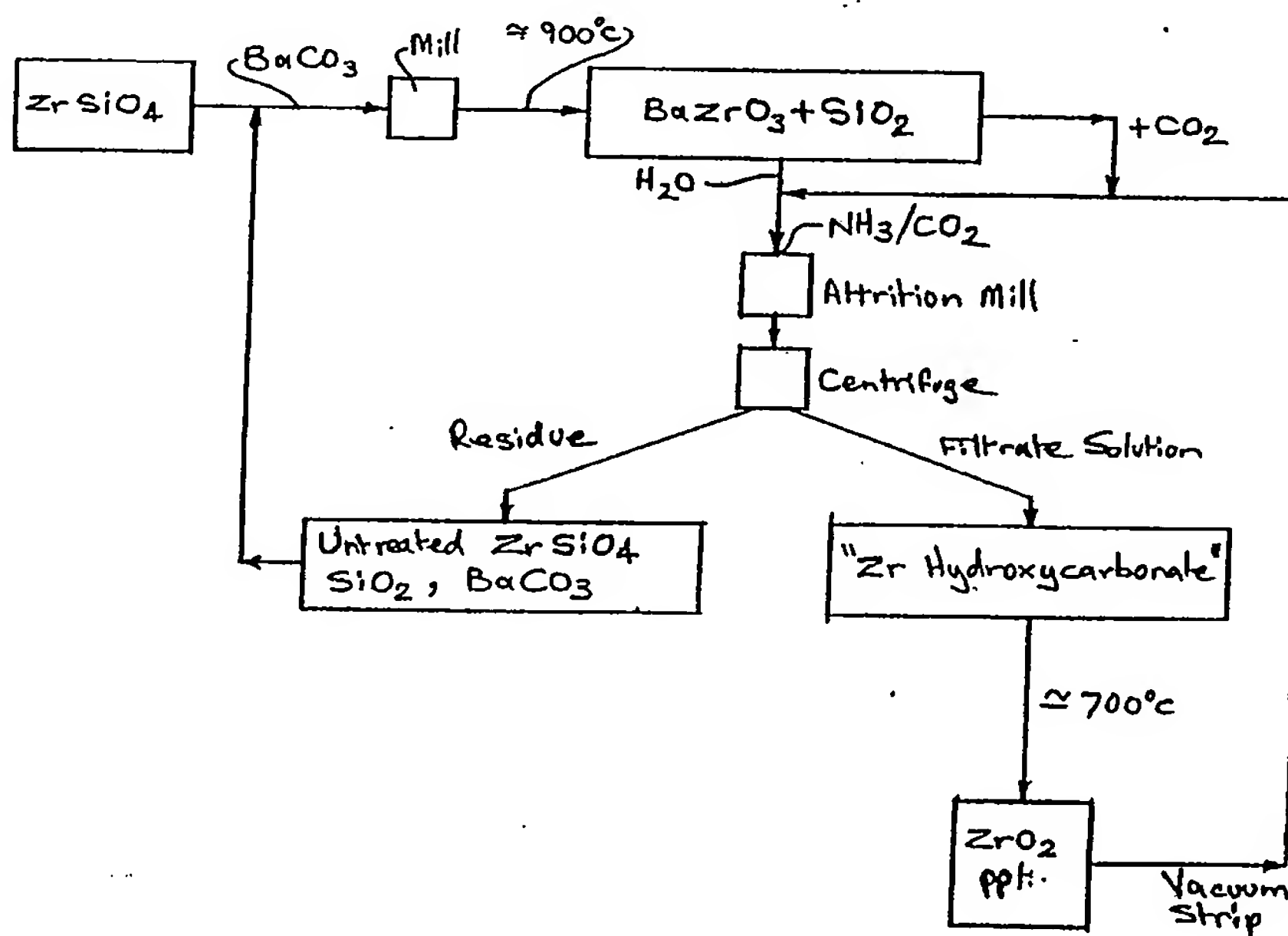
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(54) Title: ZIRCONIUM EXTRACTION



(57) Abstract

A process for producing a zirconium product, which process includes: providing a zirconium-containing material; and a leaching composition including: a source of ammonia or ammonium ions; a source of carbon dioxide (CO₂) or carbonate ions; and water; and contacting the zirconium-containing material with the leaching composition to form an aqueous slurry for a time sufficient such that a soluble zirconium leach product is produced; and isolating a leaching solution containing the soluble zirconium leach product so formed.

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ZIRCONIUM EXTRACTION

The present invention relates to a process for producing a zirconium product from zirconium containing ores, including the zirconium silicate material zircon.

5 Zirconium is an element whose metal and compounds find wide application in chemistry, metallurgy, nuclear technology, in refractories and as glazes. Zirconium principally occurs in nature as the mineral zircon, ZrSiO_4 , with lesser amounts found as baddeleyite, ZrO_2 , eudialyte
10 $(\text{Na,Ca})_6\text{ZrOH}(\text{Si}_3\text{O}_9)_2$, gittinsite $\text{CaZrSi}_2\text{O}_7$ and welognite $(\text{Sr,Ca})_3\text{Na}_2\text{Zr}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$.

Zircon is highly refractory as is shown by its geological stability. It is generally assumed to be decomposed only at high temperatures or by reaction with
15 strong reagents. Commercial methods known in the prior art to extract the zirconium content from zircon have required extreme conditions. For example,

- i) Zircon and carbon have been reacted in an electric furnace to produce a crude zirconium
20 carbo-oxynitride.
- ii) Finely ground zircon reacts with caustic soda at 600°C to afford mixtures of sodium silicate, sodium zirconate and some sodium silicozirconate.
- iii) Fusion of zircon with limestone or dolomite forms
25 a mixture of Ca (or Mg) zirconates and silicates.
- iv) Fusion of zircon with KHF_2 or KSiF_6 at 700°C produces K_2ZrF_6 .
- v) Chlorination of a mixture of zircon and carbon (or zirconium carbo-oxynitride) at $700\text{--}1200^\circ\text{C}$ affords
30 volatile $\text{ZrCl}_4 + \text{SiCl}_4$.
- vi) Thermal dissociation of zircon at $>1650^\circ\text{C}$ in a plasma produces zirconia and cristobalite, rapid quenching of the mixture and leaching with hot sodium hydroxide removes the silica as NaSiO_3 .

35 These prior art methods suffer from various disadvantages including:

- i) High temperatures and energy inefficient processing are required.
- ii) Highly reactive reagents, such as molten NaOH ,

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gaseous chlorine or potassium hydrogen fluoride are employed.

iii) Considerable further downstream processing is required to afford reasonably pure zirconia.

5 Thus, complex and expensive processing plant is required to withstand the processing conditions and the number of necessary separate steps.

Further, it has been known in the prior art that leaching, using compounds in the $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ system, 10 can be employed to extract non-ferrous metals from their ores (Hewedi, M.A. and Engle, L.F., Proc. Internat. Symp. on Hydrometallurgy, Chicago, Illinois, United States of America, 25/2-1/3/1973, pp 806-858). However, none of the ores treated have been highly or even moderately 15 refractory nor have the elements to which the disclosure relates been difficult to isolate by competing routes. Thus, such extractions have been limited to the amine or mixed amine/carbonate complexes of Cu, Ni, Co, Mn, Zn, Ga, In, U and Be.

20 It has also been reported in the prior art in United States Patent 3,0418,073 (National Lead Company), that ammonium carbonate solutions may extract the Zr content from BaZrO_3 , with the formation of $(\text{NH}_4)_3[\text{Zr}(\text{OH})(\text{CO}_3)_3]$.

25 Accordingly, it is an object of the present invention to overcome, or at least alleviate, one or more of the difficulties or deficiencies related to the prior art.

Accordingly, in a first aspect, there is provided 30 a process for producing a zirconium product, which process includes

providing

a zirconium-containing material; and
a leaching composition including

35 a source of ammonia or ammonium ions;
a source of carbon dioxide (CO_2) or
carbonate ions; and
water; and

contacting the zirconium-containing material with

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the leaching composition to form an aqueous slurry for a time sufficient such that a soluble zirconium leach product is produced; and

isolating a leaching solution containing the zirconium leach product so formed.

Accordingly, zircon and other binary (or multinary) oxides of zirconium react with aqueous solutions of a leaching agent derived from ammonium carbonate or related compounds, to dissolve the zirconium. This is very surprising in view of the highly unreactive nature usually ascribed to zircon.

The zirconium-containing material may be a zirconium-containing mineral or mineral ore. The zirconium-containing material may be a zirconium compound or complex. The zirconium-containing material may be selected from zircon, eudialyte, gittinsite or other silicates, or zirconates or mixtures thereof. For example those derived from one or more of the alkaline earths (Mg, Ca, Ba, Sr), iron, rare earths, manganese, copper or aluminium.

It has been found that improved yields may be achieved if the zirconium-containing material is initially converted to a zirconate form. Accordingly in a preferred aspect the process according to the present invention may include the preliminary step of

providing

a zirconium-containing material, and
an alkaline earth metal salt,

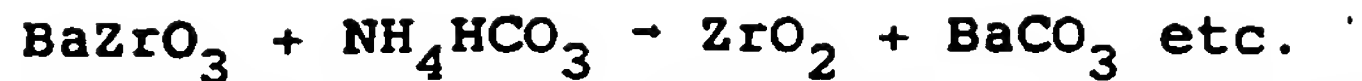
contacting the zirconium material and metal salt at elevated temperatures to form an alkaline earth metal zirconate.

Preferably the zirconium-containing material which is subjected to the pretreatment is a zircon or zirconium silicate.

The alkaline earth metal salt may be a carbonate or hydroxycarbonate. For example where Barium Carbonate is used, for example with zirconium silicate, the reaction sequence becomes



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The preliminary reaction may be conducted in the range of approximately 500°C to 1600°C, preferably approximately 750°C to 1200°C. The preliminary reaction
5 may continue for from approximately 1 to 24 hours.

The zirconium-containing phases may contain varying amounts of impurities, such as Hf, Th, U, other actinides, Y, Pb, W, Mo, Nb, Ta or Ti, either in solid solution or as a discrete amorphous or crystalline phase.

10 The particle size of the Zr-containing material may be selected to improve the efficiency of the process according to the present invention. Relatively small particles of zirconium-containing material are preferred generally below approximately 100 microns in average
15 diameter and more preferably below 50 microns have been found to be suitable.

Accordingly, in a preferred aspect of the present invention, the process further includes

20 subjecting the zirconium-containing material to a size reduction step prior to or simultaneously with the leaching step such that the average diameter of the particles is below approximately 100 micron, preferably below approximately 50 microns.

25 The size reduction step may include a crushing and/or grinding step. The size reduction step may include a milling process. Attrition milling is preferred.

The size reduction step may be conducted prior to, or simultaneously with, the leaching step. The size reduction may be preferably achieved in situ by performing
30 the milling process and leaching simultaneously.

The source of ammonium ions may be selected from ammonium compounds such as ammonium carbonate, ammonium bicarbonate, ammonium carbamate, or mixtures thereof. The source of ammonia may be aqueous or free ammonia.

35 The source of carbonate ions may similarly be selected from ammonium compounds such as ammonium carbonate, ammonium bicarbonate or ammonium carbamate, or mixtures thereof. The source of carbon dioxide may be free carbon dioxide or carbonic acid.

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A suitable leaching solution includes an aqueous ammonium bicarbonate solution wherein the ammonium bicarbonate is added to water in the ratio of approximately 1-200 grams per litre, preferably in the ratio of 40-120 grams per litre and most preferably in the ratio of 70-100 grams per litre; an aqueous ammonium carbamate solution wherein the ammonium carbamate is added to water in the ratio of approximately 1-200 grams per litre, preferably in the ratio of 40-120 grams per litre and most preferably in the ratio of 70-100 grams per litre; or a mixture of ammonium bicarbonate and ammonium carbamate in a weight ratio of approximately 10:1 to 1:10, preferably approximately 5:1. The leaching slurry may contain undissolved ammonium bicarbonate and/or ammonium carbamate. The presence of an excess of undissolved material is not necessarily detrimental to the leaching process.

The source of ammonium ions and/or the source of carbonate ions may be provided as pure solids or as mixtures, or may be generated in situ. For example, reactions may be generated with appropriate proportions of ammonia and carbon dioxide with water.

The source of ammonium ions and the source of carbonate ions may be present in any suitable relative amounts. The ratio of contained NH_3 to CO_2 may be in the range of approximately 100:1 to 1:100 by weight, preferably approximately 5:1 to 1:5.

The source of ammonium ions and the source of carbonate ions may be present in the aqueous slurry in any suitable amounts. The components of the leaching composition may be present in the aqueous slurry such that the concentration thereof is sufficiently high to ensure rapid reaction with the zirconium-containing material and/or to provide at least sufficient stability of the dissolved zirconium leach product. The ratio of the leaching composition to the zirconium-containing material may be such that the molecular ratio of CO_2 to Zr is at least approximately 1:1.

Preferably, the weight ratio of total carbon

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dioxide and carbonate, latter expressed as an equivalent weight of carbon dioxide, contained in the leaching slurry, may be in the range of approximately 0.5-100 grams, more preferably in the range 1-10 grams and most preferably in the range 2-5 grams per gram of zirconium contained in the material to be leached.

The leaching step of the process according to the present invention may be conducted at any suitable temperatures. Temperatures in the range of 0°C to approximately 200°C may be used. The temperature during the leachings step of the process should be preferably high enough to ensure rapid reaction with the zirconium-containing material, but low enough to ensure that decomposition of the dissolved zirconium leach product is minimised. Temperatures in the range of approximately 5°C to 50°C, preferably approximately 20°C to 25°C, have been found to be suitable.

The process may be conducted in any suitable conventional manner, including utilising batch processing in opened or closed vessels including autoclaves or continuous processing. The process according to the present invention may be conducted under pressures ranging from approximately atmospheric to approximately 100 MPa above atmospheric, preferably from approximately 10 to 50MPa.

The process according to the present invention may continue for a time sufficient for the zirconium-containing complex to be formed. The process may continue for approximately 12 to 48 hours, preferably approximately 15 to 24 hours.

The leaching composition utilised in the process according to the present invention may preferably include secondary components. Secondary components which alter the thermal stability or solubility of the zirconium-containing complex in the aqueous slurry and/or preferentially separate any zirconium phase formed from an impurity phase or phases, may be used.

Secondary components which may be included in the leaching solution may be selected from the free acids,

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salts or esters of phosphoric, phosphorous, sulphuric, sulphurous, citric, oxalic, benzoic, acetic or higher carboxylic, alkyl- or arylphosphonic or -sulphonic acids or the free acids or salts of the halides F^- , Cl^- , Br^- , I^- or pseudohalides CN^- , OCN^- , SCN^- or combinations thereof. Alkali metal or alkaline earth metal salts of the halides or pseudohalides are preferred. An alkali metal thiocyanate, e.g. KSCN is preferred. The secondary components may be added as pure solids or liquids, as diluted solutions or generated in situ, such as by reaction of free acids with NH_3 or the major leachant solution.

The secondary components may be present in the leaching composition in amounts of 0 to approximately 50%, preferably approximately 0.1 to 5%.

The leaching solution containing the zirconium-complex may be separated from the aqueous slurry in any suitable manner. The zirconium-complex may be separated from any unreacted material or from insoluble reaction products, by filtration, flotation, centrifugation or by sedimentation.

The residue may be recycled and reacted further with fresh leaching composition, with the same or a different composition under the same or different reaction conditions as used in the original leaching reaction.

Accordingly in a preferred aspect of the present invention the process may further include

separating the zirconium leach product from the leaching solution, and recycling the residue of the separation step to the leaching step.

Accordingly in a further aspect of the present invention, the process may further include

contacting the residue and an alkaline earth metal salt at elevated temperature to form an alkaline earth metal product; and

recycling the alkaline earth metal product to the leaching step.

The alkaline earth metal salt may be a carbonate

or hydroxy carbonate. Barium carbonate is preferred. The reaction may be conducted at a temperature in the range of approximately 500°C to 1600°C, preferably approximately 750°C to 1200°C.

5 In a preferred aspect of the present invention, the process of producing a zirconium product may further include

subjecting the zirconium leach product to a decomposition step.

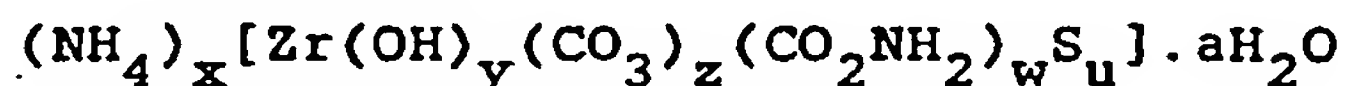
10 A zirconium-containing product, for example zirconia or other zirconium-containing solids may be isolated from the leaching solution by thermal decomposition whilst still in solution, of zirconium leach product.

15 The zirconium-containing product may be precipitated out by seeding the solution with zirconium crystals.

Alternatively, the zirconium-containing product may be utilised in solution form, for example to form
20 cotaings on a substrate.

The zirconium-containing product may be subjected to further reactions, e.g. either in solution form or after extraction to form mixed metal oxides as described in Australian Patent Application PK 2626 the entire
25 disclosure of which is incorporated herein by reference.

In a further aspect of the present invention, there is provided a soluble zirconium-containing complex having the composition:



30 wherein $x = \text{a number from 0 to 4}$

$$y + 2z + 2w + u = 4 + x$$

$S = \text{mono-, di-, or trivalent anion}$

$a = \text{a number from 0 to 10}$

$x, z, y, w, u, s \text{ and } a \text{ may not be integers}$

35 For example, the soluble zirconium-complex may have the formula $(\text{NH}_4)_3[\text{Zr}(\text{OH})(\text{CO}_3)_3]$.

Decomposition of the zirconium-containing species may result in formation of free gaseous NH_3 , CO_2 or other components of the original leaching solution; these

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may be returned to the reaction process. After removal of some or all of the soluble zirconium-complex, the leaching solution may be recycled for use with a fresh charge of zircon or other zirconium-containing material.

5 In the following description the invention will be more fully described with reference to the accompanying example. It should be understood, however, that the following description is illustrative only and should not be taken in any way as a restriction on the generality of
10 the invention described above.

EXAMPLE 1

A mixture of zircon (18.3 g), of average particle size 50 microns, and commercial "ammonium bicarbonate" (47.5 g) (a mixture of NH_4HCO_3 and $\text{NH}_4\text{CO}_2\text{NH}_2$ in
15 approximate ratio of 5:1) was stirred in water (54 ml) at room temperature for 20 hours in an attrition mill with 1 mm diameter PSZ balls. After that period the slurry was filtered and the residue analysed to reveal silica and some unreacted zircon. The filtrate was evaporated to
20 dryness at 120°C and heated to 700°C for 30 min. The XRD of the white residue, which weighed about 2 g, showed it to contain crystalline tetragonal zirconia, by comparison with an authentic sample.

EXAMPLE 2

25 Zircon powder (ZrSiO_4) (36.6 g) and barium carbonate (40 g) were ground together in a ring mill for 15 minutes. The mixture was then placed in a crucible and heated in air (900°C, 4 h). An XRD of the resulting powder showed about 40% of the zircon had been converted
30 into BaZrO_3 . A 50 g sample of this mixture was treated with ammonium carbonate (95 g) in water (95 ml) in an attrition mill (200 g of 1 mm PSZ beads) for 24 h. After that period the slurry was filtered and the residue analysed to reveal the complete disappearance of the
35 BaZrO_3 . The filtrate was evaporated to dryness at 120°C and heated to 700°C for 30 min. The XRD of the white residue, which weighed 9g, showed it to be crystalline tetragonal zirconia, by comparison with an authentic sample.

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A recycle system utilising this process is schematically illustrated in Figure 1.

Finally, it is to be understood that various other modifications and/or alterations may be made without departing from the spirit of the present invention as outlined herein.

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Claims

1. A process for producing a zirconium product, which process includes
providing
5 a zirconium-containing material; and
a leaching composition including
a source of ammonia or ammonium ions;
a source of carbon dioxide (CO_2) or
carbonate ions; and
10 water; and
contacting the zirconium-containing material with
the leaching composition to form an aqueous slurry for a
time sufficient such that a soluble zirconium leach
product is produced; and
15 isolating a leaching solution containing the
soluble zirconium leach product so formed.
2. A process according to claim 1, wherein the
zirconium-containing material is selected from zircon,
eudialyte, gittinsite, other silicates, or zirconates, or
20 mixtures thereof.
3. A process according to claim 2, wherein the
zirconium-containing material is an alkaline earth metal
zirconate.
4. A process according to claim 2, including the
25 preliminary step of
providing
a zirconium-containing material, and
an alkaline earth metal salt,
contacting the zircon-containing material and
30 metal salt at elevated temperatures to form an alkaline
earth metal zirconate.
5. A process according to claim 4 wherein the
zirconium-containing material which is subjected to the
pretreatment reaction is a zircon or zirconium silicate
35 and the alkaline earth metal salt is barium carbonate.
6. A process according to claim 5 wherein the
preliminary reaction is conducted at a temperature in the
range of approximately 500°C to 1600°C .
7. A process according to claim 1, further including

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subjecting the zirconium-containing material to a size reduction step prior to or simultaneously with the leaching step such that the average diameter of the particles is below approximately 100 micron.

5 8. A process according to claim 7 wherein the zirconium-containing material is subjected to a milling process simultaneously with the leaching step.

9. A process according to claim 1, wherein the source of ammonium ions is selected from aqueous ammonia,
10 ammonium carbonate, ammonium bicarbonate, ammonium carbamate or mixtures thereof; and

the source of carbonate ions is selected from ammonium carbonate, ammonium bicarbonate, ammonium carbamate or mixtures thereof.

15 10. A process according to claim 1, wherein the ratio of the leaching composition to the zirconium-containing material is such that the molecular ratio of CO_2 to Zr is at least approximately 1:1.

11. A process according to claim 10, wherein the
20 leaching composition includes secondary components which alter the thermal stability or solubility of the zirconium-containing complex in the aqueous slurry and/or preferentially separate the zirconium phase formed from an impurity phase or phases.

25 12. A process according to claim 11, wherein the secondary components are selected from the free acids, salts or esters of phosphoric, phosphorous, sulphuric, sulphurous, citric, oxalic, benzoic, acetic or higher carboxylic, alkyl- or arylphosphonic or -sulphonic acids
30 or the free acids or salts of the halides F^- , Cl^- , Br^- , I^- or pseudohalides CN^- , OCN^- , SCN^- or combinations thereof.

13. A process according to claim 1 further including
separating the zirconium leach product from the
35 leaching solution, and

recycling the residue of the separation step to the leaching step.

14. A process according to claim 1, further including contacting the residue and an alkaline earth metal

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salt at elevated temperature to form an alkaline earth metal product; and

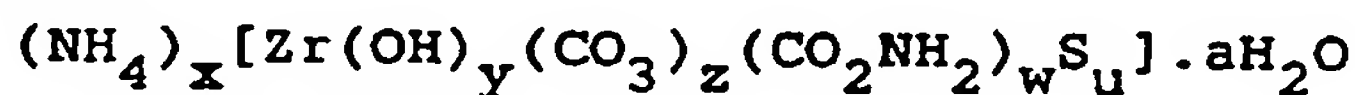
recycling the alkaline earth metal product to the leaching step.

5 15. A process according to claim 14 wherein the residue is contacted with barium carbonate at a temperature in the range of approximately 500°C to 1600°C.

16. A process according to claim 1, further including
10 subjecting the zirconium leach product to a decomposition step.

17. A process according to claim 16, wherein the zirconium leach product is subjected to thermal decomposition to form zirconia or other zirconium-containing solid.

15 18. A soluble zirconium-containing complex having the composition:



wherein $x = \text{a number from 0 to 4}$

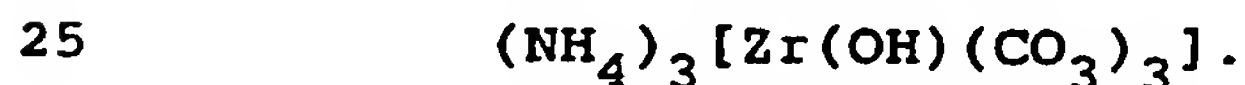
$$y + 2z + 2w + u = 4 + x$$

20 $S = \text{mono-, di-, or trivalent anion}$

$a = \text{a number from 0 to 10}$

x, z, y, w, u, s and a may not be integers.

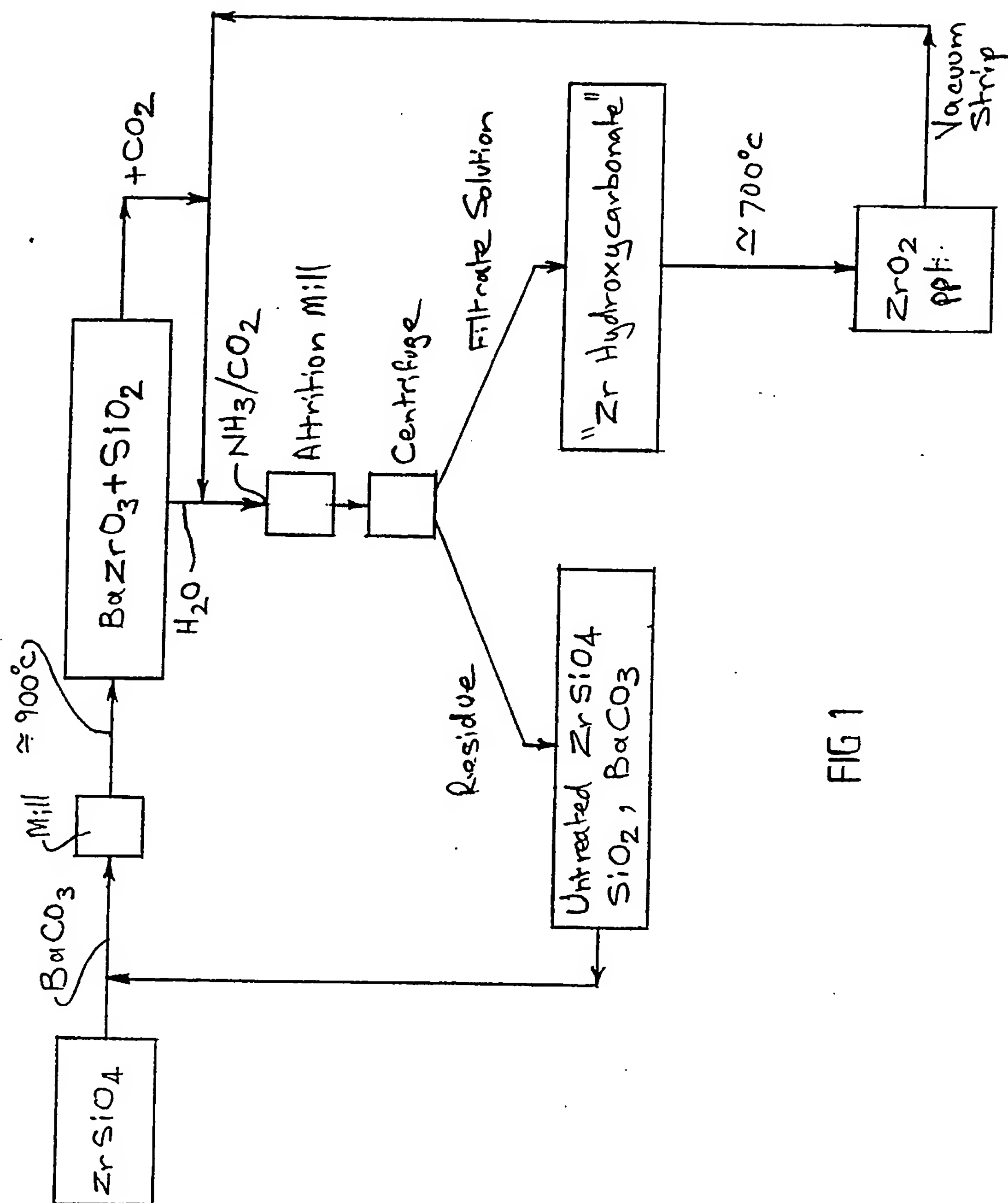
19. A soluble zirconium-containing complex according to claim 18, having the formula



20. A process according to claim 1, substantially as hereinbefore described with reference to any one of the examples.


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INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU92/00436

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁵ C22B 3/14 // C22B 34:14 According to International Patent Classification (IPC) or to both national classification and IPC																						
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC: C22B 3/00, 34/14, 3/14, 61/02. Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC as above. Electronic data base consulted during the international search (name of data base, and where practicable, search terms used) DERWENT and JAPIO: C22B 3/00 and zirconium and (ammonia or ammonium) and (carbon)dioxide or carbonate or bicarbonate or carbamate or carbonic).																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.																				
X	US,A, 2847300 (PAULL) 12 August 1958 (12.08.58) Claims 1-12.	1,2,7,8,13,16.																				
A	US,A, 3811871 (TAYLOR) 21 May 1974 (21.05.74) Abstract, Examples 1-4.	1-17, 20.																				
A	US,A, 3252920 (GOREN) 24 May 1966 (24.05.66) Claim 1	1-17, 20.																				
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Date of the actual completion of the international search 24 November 1992 (24.11.92)		Date of mailing of the international search report 30 Nov 1992 (30. 11. 92)																				
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
A	US,A, 2837406 (SCHAUFELBERGER) 3 June 1958 (03.06.58) Column 2, lines 10-37.	1-17, 20.
A	US,A, 2670271 (THOMSEN) 23 February 1954 (23.02.54) Claims 1 and 2.	1-17, 20.
A	US,A, 2698220 (ERSKINE) 28 December 1954 (28.12.54) Claims 1-7.	1-17, 20.
A	EP,A, 154448 (IRON ORE COMPANY OF CANADA) 11 September 1985 (11.09.85) Abstract.	1-17, 20.

INTERNATIONAL SEARCH REPORT
Information on patent family mem:

International application No.
PCT/AU92/00436

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
US	3811871	US	3784593	US	3912498
EP	154448	AU	38987/85	JP	60255621
		ZA	8501295	NO	850670
END OF ANNEX					